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Effect of Environmental Conditions and Additive Clay-Particles on Properties of Epoxy–Clay Nanocomposites: A Review

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ABSTRACT

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Introduction:

In the last years, the development of polymer nanocomposites was based on using different types of polymers such as epoxy as a matrix and nanoparticles such as clays as an additive material. These types of nanocomposite materials have received noteworthy consideration because of the considerable perfections to improve their properties including mechanical behaviour, and thermal enhancement compare with the properties of the individual polymer before the addition of nanomaterial [1-3]. The nanocomposite systems have great benefits of applications. These advantages made nanocomposites to become an important research area. There are many reasons for these advantages; one is their great mechanical characterizations. The concluded distribution of nano clay layers within polymeric matrices improves the amount of presented additive components.

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In the previous few decades, nanocomposites including epoxy risen-clay nanoparticles systems were proven possibility to have developed properties over original matrices. The environmental conditions, which surround the nanocomposite systems, have a scientific effect on their properties during using them for a long time. Therefore, studying the effect of environmental conditions associated with adding clay nanoparticles on the properties of nanocomposites is important to achieve the requirement of the applications. Nanocomposites are utilized in substructure applications and experience mechanical loads and thermal effects when they are exposed to environmental surrounding conditions which are included electromagnetic ultraviolet (UV) energy, humidity or wetness, water absorbance, and some alkaline solutions. These materials are showed their ability to barrier the environmental surrounding effects. Diffuse the liquids in nanocomposite systems has been established by different approaches (models). The review study involves the research effort performed on nanocomposite (epoxy-clay nanoparticles) under some environmental issues such as moisture or water properties and their diffusion into nanocomposite, exposure to various environments: radiation in the range of UV, temperature, and humidity. The current developments are additionally discussed.

> Mechanical properties have been improved due to the connection between the higher average surface section of the clay nano-particles with the used polymeric matrices [4-6]. Another general benefit of the nanocomposite systems is their greater barrier property. A resistant clay nano-layer influences an indirect way of the permeating transversion used system. It is informed that gas penetrability via polymeric films was diminished about 50–500 times through fillings of clay nanoparticles. The pertinent studies on clay nanocomposite deal with particular gases such as N₂, O₂, and Co₂ barrier samples, for example, packaged food and gaseous drinks. Further used for some purposes involve gas containers and coats [7].

> Basically, epoxy resins have been used as matrix materials which are shown attractive properties such as mechanical, great heat distortion, stability thermally, and environmental stability. Consequently, epoxy, as a matrix material, has a thermoset behavior compared with other polymers, this matrix can be reinforced with glass fibers and particles and thus can be a good anticorrosion layer [8]. In general, Clays are materials that consist of some basic elements such

as (magnesium, aluminium, silicon, hydroxyl, and oxygen) besides several linked cations. These elements can be formed in aluminium or hydrous silicates. The units of ions and OH are structured into sheets as two-dimension shapes. Some clays such as minerals type, for example, can be classified as silicates in form layers or phyllo, since their structure dimension is essential, has a thickness of about1 nm silicate layers including sheets of silica and alumina which are linked and composed in several magnitudes and fixed on the upper of each other in a means through adjustable interlayer areas. The minerals type is categorized into three various forms constructed on the concentration percentage of alumina to silica sheet [9-11].

Clay materials can be classified naturally into many categories; the first one is the 1:1 type. This class of clay contains two sheet minerals of a single octahedral part of alumina sheet packed together with a single tetrahedral part of silica sheet in a percentage of 1:1, these sheets are termed as dimorphic. Because of the non-existence of isomorphic replacement, these sheets do not exhibit any type of charge. A hydrogen bond is taking place to hold the layers together, this bond is holding the hydroxyl unit and oxygen unit in octahedral and tetrahedral sheets respectively, while the areas between these layers are filled via water molecules [11]. Second class of clay is 2:1 type [11]. Triple sheet minerals have occurred in this type of clay in a percentage of 2:1, two outer sheets from silica are made of a sandwich structure with one alumina sheet. This style of clay is a member of the smectite group. Accumulation of these types of layers makes to generate a Van Der Waals gap amidst the clay layers. Substitution of the isomorphic ions, in the sheet type octahedron, such as Al³⁺ with others such $(Li^+, Mg^{2+}, and Fe^{2+})$ as well as in the sheets type tetrahedron, the substitution of Si⁴⁺ by the ion of Al³⁺ , these replacements provides any layer a total negative charge, thus the cations of exchangeable metals, such as Li+, Na+, and Fe2+, which are in a counterbalance case, which are resided in the interlayer area. The third class of clay is the 2:2 type [11]. The form of this type which is named as tetramorphic type consists of 4 metallic sheets, this type can be created by the alternative concentration of tetrahedron sheets and octahedron sheets. The fourth type of clay is Montmorillonite [11]. This type is generally utilized for the formulation of nanoclay composites [12-19This type of clay has shown particular interest from other members of the smectite classifies owing to its property to illustrate large interlayer extension or expansion, as a result of its unique formation which is demonstrated in Figure 1 [11]. Sandwiched structure from tetrahedral sheets of silica covering one sheet of octahedral alumina is the main crystalline structure of montmorillonite, therefore, the atoms of apical oxygen from a sheet of tetrahedral can contribute to the octahedral type. The fifth type of clay is an organic modification [11]. In general, the clays are naturally hydrophilic. Therefore, to make them are matching with organic resins, the clay minerals surface is changed to organophilic prior before use it. The organic modifications involved the replacement of inorganic cations with salts of organic onium. This modification reasons the increase of the interlayer area which leads to rising the d spacing to a range of about 2 nm. Hence, the diffusion of polymer within the interlayer area is preferred in organic modification. The organic modification process of clay is schematically presented in Figure 2. The ions of Alkyl ammonium are mostly common meanwhile they are simply replaced with other ions located among the layers.

According to the charged density of the clay layer, the ions of Alkyl ammonium could adopt various structures among the layers of clay material. These ions decrease the electrostatic reaction presented in the layers of silicate, therefore, simplifying the diffuse of the polymer molecules within the arcades. Generally, the extended surfaceactive agent the length of the chain [11, 15]. The nanocomposite systems contain two or more different phases that contain a polymer as a matrix and distributed inorganic nanoparticles. The inorganic nanoparticles are a part of the type 2:1 phyllosilicate group [7].

The crystalline structure of this group (Figure 1) [8] involves Al or Mg (OH) (hydroxide) octahedral sheet to be in sandwich design among two sheets of silicon oxide. Their thickness is about 1 nm, and their side dimensions could be varied by nearly 30 nm towards some microns. Two features of layers type silicate are played a significant character in the manufacture of nanocomposite materials: firstly, the diffuse of silicate sheets within single layers, and

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secondly, the chemical modification of their surface out of ion-modified reactions via cations such as organic and inorganic types [7].

The alkylammonium cations work to minimize the energy of the inorganic surface, enhance the wetting property of the used polymeric matrices, and make the interlayer spaces to be longer which means swelling. Moreover, these cations play to provide operational units to interact with the polymeric matrices as well as the formation of the polymeric in situ by starting the polymerization process of their monomers [22]. Morphologically, there are four kinds of nanocomposites that are classified depending on the force of their interaction, (Figure 3) "intercalated, exfoliated, flocculated, and aggregated" [71].



Figure 1 The main structure of the crystalline phyllosilicates' group (montmorillonite) [8].



Figure 2 Schematic plot of organic modification process of clay [11].



Figure 3 Classes structures of clay-polymer nanocomposite [71].

1. Nanocomposite fabrication.

For a good distribution of nano clay particles into polymer matrices, which is important to achieve developed properties of matrices, there are three common methods are used first is melt intercalation, the second is solution intercalation, and the third is in situ polymerization.

In the first method, the basic property is the melting degree of the used polymeric matrix and is focusing on increasing the annealing temperature of matrices higher than their melting point [25-27, 29]. This method is suitable for industrial companies to manufacture nanocomposites. But it is not appropriate to manufacture thermosetting matrices, for instance, epoxy and polyester owing to their extreme viscosities as mentioned in Ref. [30, 31]. Therefore, the other methods are suitable for manufacturing these types of thermoset matrix/clay systems[28].

In the second method the basic way is to solve the epoxy matrices with a suitable solvent. Normally, the utilized solvents in this process are: "chloroform, acetone, ethanol, and methanol". In this method, many factors can be taken into account during the manufacture of nanocomposite associated with these mentioned solvents, these factors are (the polarity, evaporated temperature, and volatility) of the used solvents as well as the gradation of distribution with extreme quantities of used clays nanoparticles Ref. [27, 28, 32-34].

In the third method, the basic procedure is to mix the clay nanoparticles directly into the polymeric system. In this case, the polymeric monomer groups are distributed within the interlayers of clay nanoparticles to create intercalation formations. And finally, the polymerization mechanism can be completed by using one of the following catalysts: applied radiation, heat treatment, and diffusion Ref. [27-29, 35, 36]. Also in this method, there are different procedural requirements that are managed by heat, speed, and time of mixing process, and created shearing stress due to the parts of the mixer such as the rotor and blade, Ref. [24, 28]. Extremely research in the literature is focused on mixing clay nanoparticles with epoxy resin utilizing mechanical methods to achieve the mixing process, these methods include (a mix handle, magnetic stirrer, centrifuge way), "three-roll miller", and "ultrasonication". Occasionally, the preparation process is achieved by combining two methods to reach the required quality of produced nanocomposites.

1.1 Methods based on mechanical processes.

Mechanical techniques have been widely utilized to mix clay nanoparticles with polymeric resins. This process is easy to modify and uses a heater with suitable temperatures to decrease the viscosity of the resin as the addition of clay nanoparticles increases its viscosity and affects the mixing process by making it hard due to the addition of clay nanoparticles. One of the common mechanical methods used is the three-roll miller which is extensively used to produce intercalated and exfoliated nanocomposites. This method is involved three rolls: "feeding roll, a central roll, and an apron roll". This method is presented in Figure 4 (a). The detail of this method is presented in Ref. [27, 37].

1.2 Method based on ultrasonic waves.

Ultrasonic equipment is a vibration technique which is broadly utilized for distributing clay nanoparticles within polymer matrices. The ultrasonic probe is the main part of this tool which is used to mix clay nanoparticles resin combination. The vibrations of ultrasonic waves are created by the probe. More details are presented in Ref. [27]. This technique is illustrated in Figure 4 (b).

1.3 Method based on chemical reaction.

Some chemical manners are existing for distributing clay nanoparticles within resin matrices manufacture nanocomposites. The common to method used to produce nanocomposite is the slurry combination route [38, 39]. In this manner, the clay nanoparticles are dissolved by deionizing water and using stirring and sonication techniques to increase the dissolved process. Then, an amount of acetone is added to the solution to make a clay nanoparticles and ace-tone slurry mixture. This mixture is obeyed to blend way with polymer resin and to remove the acetone a vacuum furnace is used to evaporate it. After that, the prepared mixture is treated to manufacture the nanocomposite. The main procedure of the slurry process is schematically represented in Figure 4 (c). More details are presented in Ref. [27].





2. Environmental effects

The reinforced materials, such as fibers, flakes, and particles or nanoparticles, of composites or nanocomposite utilized in substructure applications experience mechanical loads and thermal effects during that they are exposed to environmental

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surrounding conditions which included are electromagnetic ultraviolet (UV) energy, humidity, or water absorbance, and some alkaline wetness, solutions salts [40]. These environmental or conditions could affect the properties of nanocomposites in a positive or negative way. These effects can result in the measured data. Some environmental conditions and their effects on the nanocomposite system are presented in Figure 5.





Figure 5 (a), (b) Flexure modulus and (c),(d) flexure strength for epoxy and nanocomposites system are plotted to exposure time in hours, exposed to environmental exposure via heat temperature and humidity linked with UV waves and concentration. This data is replotted from table 3 and 4 of Ref. [40].

From Figures 5 (a), (b), (c), and (d) the effect of some environmental conditions such as shared temperature-humidity and shared UV radiationcondensation on the calculated amounts of flexure modulus and flexure strength under exposure period, for two materials: neat epoxy and nanocomposites of (epoxy-clay). However, some conditions do not affect the result, for example, the environmental humidity has led to no significant variation in flexure modulus for both materials figure (a). In reality, it seems that the modulus slightly rises caused by the moisture absorption [40].

While during the same exposure duration under experience to UV energy and concentration, the flexure modulus is slightly reduced for together materials. The erosion of epoxy due to interactive epoxy degradation has led to a decrease in the modulus. To compare the result for both materials the reduction in modulus is marginally larger for the neat epoxy from the nanocomposite, which designates that the filling of clay has led to improved durability. On the other hand, flexure strength, for all materials suffers degradation in strength while subjected to all environmental conditions Figure (c) and (d). From all conditions, experience with shared UV waves and concentration has led up to a decline in flexural strength. However, the reduction is smaller for nanocomposite, to conclude that the addition of clay nanoparticles has led to improvement in the resistance the degradation due to environmental effects.

2.1 Degradation of Surface by Environmental Conditions

Experience of polymer resins such as epoxy to environmental conditions such as UV energy has drawbacks to the creation of microcracks, that can be served as local positions for extra substance degradation, particularly during the "synergistic degradation" processes are effective. In this study, the surfaces of prepared samples upper (the nanocomposite based on epoxy) were checked under the same exposure durations. The examined samples under UV energy and condensation began showing surface degradation about 14 days of exposure. Therefore, more exposure time leads to more degradation within the surface was detected [40].

Firstly, generated tiny cracks are created near the surface of the sample then when the exposure time is increased, the cracks grow to be bigger in size and quantity. By increasing the time of exposure, curved "dome-shape" depressions have been detected on certain regions of the sample's surface area. The depressions altered in size which can be seen by the naked eye. Therefore, the behaviour of degradation of the surface was not regular all over the section.

Micro sizes of cracks were mainly detected close to the center of examined samples, but type of dimples was created near to the edges. Hence, it is likely that microcracks are dominated variations of surface because of "inherent material the degradation", but the dimples could be resulted due to "physicochemical the interaction" among the specimen holders [40].

Relative or percentage expansion in d-spacing which is denoted as a fraction of the sample after swelling and original d-spacing of the epoxy Figure 6. Both forms of organic variation considerably encourage intercalation of the epoxide among silicate sheets as suggested by the rise in the d- space as result of swelling. The organoclay type A had the maximum rise which suggests the greatest compatibility of the used clay within the epoxy because of the existence of the "hydroxyl functionality". Additionally, hydroxyl classes could interact along with epoxy components of the prepolymer which leads connection the chains of used polymer (epoxy) with the surface of the clay material, hence, increasing clay structure. While organoclay type D was showed a lowest growth in the interlamellar space which could be due to high ranking of "hydrophobicity" within the type D [41]. In this work, they denoted Clay types (A, B, C, and mentions D) that to ("methyloctadecyl, dimethyloctadecylphenyl, dimethyloctadecyloctyl, and methyldioctadecyl") ammonium chlorides respectively [41].



Figure 6 D- spacing for different types of clay (A, B, C, and D) [41].



Figure 7 Main mechanical properties of nanocomposites having nanoclay about 6 wt % [41].

Tensile results of treated structures including a 6 wt % percentage from organic-clay material were determined, which is demonstrated in Figure 7. By comparing the result with the neat resin, all composite structures illustrate significant expansion in extension at the break. The concatenation of reduction the elongation at break coincides with the intercalation strength of manufactured organoclay and hence is concerning to the possibility of professionally exfoliating a clay material in the epoxy matrix.

Nanolayers, from exfoliated clay, have an extremely great certain surface area and the conformation influences of the galleried ions on epoxy at the clay-epoxy composite interface may promote the greater softness of composites involving clay platelets such as exfoliated or partly exfoliated. The Young's modulus of the composite type A is slightly reduced due to the plasticising result of modifier A, which is reliable with the decline of Tg. As a consequence of the contribution of modifier A in the treating of epoxy, the combination of modifier A could be shown an additional substantial influence on Tg of epoxy resin [41].

2.2 Effect of nanoclay on diffusion process of liquid in matrix material

Exposing the nanocomposite samples to environmental effects such as water as well as raw oil to examine the impact of additional nanoparticles of clay on diffusion and quantity of fluid uptake. It is found that addition of nanoclay has improved the barrier ability of the matrix material (epoxy). Anywhere, addition of 1% from nanoclay particles reduced the diffusion to 51% and the highest water uptake to 8% [8].

The diffusion process of liquid such as water in neat epoxy was good projected by Fickian model, but the Langmuir model was well matched to the nanocomposites [8]. Some research works were indicated that the liquid uptake reduces the properties of epoxy-nano composites [42- 44]. The liquid absorption such as water in matrix material is connected to the presence of "molecule-size holes" as well as the rapport of water and polar units of polymers [45].

Absorbed molecules of the used liquid behave as an effective plasticizer for treated epoxy matrixes thus decreasing their properties. The influence of additive nanoclay on diffusion and liquid uptake of matrix materials has been extensively researched, contrary findings have been registered in references [46–56]. Certain searches determined that water diffusion in matrix materials declined as the clay particles content are going up [47, 49–51] whereas some studies indicated rise in diffusivity as the clay amount is increased [53]. While the decline in highest water uptake caused by more addition of clay particles was confirmed by certain investigators [47, 53, 56], however some researchers stated an increase in the highest water uptake due to the adding of clay particles [49, 52, 54]. As reported in Ref. [49], the decrease of absorbed liquid in matrix materials owing to the additive of nanoclay is helped to inhibit the degradation which result by water amount and thus enhance performing of nanocomposites to use for long time.

2.3 Effect of absorbed Water

Studying the water absorption in epoxy matrix can be explained depending on the percentage water uptake which decreased due to present the silyl unit into epoxy matrix and owing to its essential natural hydrophobic (Table 1). More, the combination of surface modified clay particles within Si-epoxy matrix can be led to diminish the ratio of water uptake owing to the lessening in permeability performance which impacted by the creation of exfoliated nanocomposites system [57]. Also, addition the unsaturated polyester (UP) to epoxy matrix leads to reduce the ratio water uptake as presented in Ref. [58]. Further, adding the clay particles to this system (UP and epoxy) leads to diminish the ratio water uptake.

2.3.1Water Uptake Model

The diffusion mechanism of diffuse the liquid such as water in nanocomposite systems has been established by different approaches or models [59– 62]. One of these approaches is "Fickian model" which is usually utilised for diffusion as "individualfree-phase", owing to its easiness, however, diffusion of liquid such as water in some matrix systems does not obey to Fickian model [61]. Therefore, the "Langmuir model" of diffusing (LMD) can be suitable to study the diffusion nanocomposite systems [61]. In this type of model, amount of absorbed water molecules is assumed to be bound and some have motion [8]. The basis of the Fickian model is the second law of Fick with diffusivity to be constant. the assumption idea based on this model is assumed that

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all molecules of water can be diffused freely in the matrix material, therefore the relation of molecules' diffusion with their concentration is assumed to behave independently. The second law of Fick, which expresses the behaviour of diffusion with a fixed diffusion (D) in one dimension (x) over an infinite plate with the thickness (h) follows the relation [62].

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \tag{1}$$

Where c represents the concentration and t represents the time.

The Langmuir model expected that the water is assumed to occur in two sets: the first is for molecules which diffuse freely in the matrix material and the second is designed for trapped molecules. At a certain time and place, free molecules can be diffused per probability (c), in the matrix, moving with diffusion D is connected or trapped in the matrix materials, whereas others have probability (a) of the hindered molecules with mobility. Therefore, the fraction of weight gain can be stated as following relation [62].

$$\frac{M_t}{M_s} = 1 - \frac{\gamma}{\gamma + \alpha} e^{-\alpha t} - \frac{8}{\pi^2} \frac{\alpha}{\alpha + \gamma} \sum_{0}^{\infty} \frac{1}{(2n+1)^2} x \exp\{-\left[\frac{\pi(2n+1)}{h}\right]^2 Dt\}$$
(2)

2.3.2Influence of liquids Uptake on glass transition temperature Tg.

The (Tg) temperature, of both materials of the nanocomposites system, can be affected by clay particle filling associated without exposure and with exposure to liquid uptake, the result is illustrated in Figure 8. The values of Tg, for samples without exposure, were reduced almost in a linear relation with rising clay particles filling. This decline in Tg has been recognized as diminished crosslinking density with rising clay filling in the nanocomposite system [63]. The decrease in Tg is attributed to the lack of the surrounded entanglements presented at the interface as well as to the influences of clay platelet as a barrier that could decline the crosslink concentration of treated epoxy [64]. Due to the exposure process of epoxy by water, the Tg was degraded by about 30 and was 23 C for oil uptake. This decrease in Tg in the case of water uptake was the typical similarity with consequences informed by some investigators [59, 65]. While, for the liquid uptake, the Tg has degraded in the case of the

that the decline in Tg in the case of nanocomposites system including about 2% clay particles was 18 oC for water and 9 oC for used oil. The magnitude of the influence of liquid uptake on Tg is reduced with rising the percentage of clay filling, for a system of nanocomposite containing 5 per cent of clay filling, the fall in Tg owing to water was 12 °C while for oil uptake was just 3 °C [8]. Therefore, the glass transition temperature is influenced by the effect of clay content [23]. Again, because of the exposure time, the degradation in Tg could be outlined to the plasticizing influence of minor separated molecules of both waters as well as crude oil that were absorbed within the epoxy. The declines in Tg values appear to have related to the greatest uptake, which describes the diminished decline in Tg in the case of specimens exposed to both of crude oil and water [8].

nanocomposite system less than the epoxy. It is found



Figure 8 Alternative of Tg due to filling of clay into nanocomposites under exposure to liquids [8].

From Ref. [57], it is found that by using the DSC technique the result of thermograms has been recorded for both of Si-epoxy matrix and the nanoclay composites. The Tg and curing response of both matrixes were investigated to analyse the influence of clay particle surface modification and filling on matrix resin material. For this system, the curing response of the Si-epoxy matrix including "curing agent DDM" was stated by Ref. [66]. The addition of silicon elements into the epoxy matrix type (DGEBA) improves the reaction of the rings of epoxy resin to the DDM [66]. The electronic concentration of the oxirane ring is decreased due to the increased "electronegativity" of the silicon element, thus leading to the rise of the epoxy rings open mechanism. The presence of silyl units within the epoxy resin lessened the Tg. It is found that the values of Tg in the case of pure epoxy are higher than those of the Si-epoxy system. The obtained result is owing to the existence of stretchy linkage of "Si—O—Ph" into the body of the Si-epoxy matrix. In addition, the integration of silicon units within the epoxy matrix could affect the compounds of epoxy resin with twice aryl units like bulky pendants structure. These units produce additional free volume owing to the throng and cut down the density of the crosslinking process of the matrix systems and leading to reducing of Tg quantity [66].

The mixture of unmodified clay within the system of Si-epoxy matrix improves the glass transition temperature (Tg) by 7°C by adding the clay about 5wt%. Increasing the addition of unmodified clay to 7wt% decreases the value of Tg by about 152°C [57].

Table 1 Heat distortion, Tg, and water uptake result of nanocomposite system [57].

Si-epoxy/clay w/w	Heat distortion temperature (C)	Glass transi- tion tempera- ture (C)		Water absorp- tion (%) 25 C, 48 h
		DSC	DMA	
Е	154	162	165	0.3
SE	135	146	148	0.11
SE A1	143	148	150	0.10
SE A3	147	151	153	0.09
SE A5	150	154	155	0.8
SE A7	145	147	152	0.07
SE B1	139	141	146	0.10
SE _{B3}	134	139	143	0.09
SE b5	130	136	139	0.07
SE b7	128	132	137	0.06
SE c1	135	139	142	0.08
SE c3	127	137	136	0.06
SE C5	125	134	132	0.05
SE c7	119	125	127	0.04

The consequences of the impact of clay filling and humidity amount on Tg are presented in Figure 9. From this figure, the Tg of NC stays closely constant with about one atmosphere and has dissimilar values with altered filler content [67].



Figure 9 Plotted of Tg via relative humidity (RH) [67].

This decrease designates a probable minor crosslink density surrounding particles of clay filling, which could owe to the disturbing influences of the clay particles [68, 69] as well as the epoxy chains are interacted with the particle's surface leading to the result of an interphase creation among the layers of silicate [7, 37, 70]. The addition of 1% from nanoclay particles to the epoxy matrix has led to reducing the glass transition temperature, Tg, to about 8% [8]. Generally, in the majority of the epoxy matrix, the Tg is lowered by 20 °C for every 1% moisture [71, 72]. Three systems [73]; "(1) unmodified epoxy, (2) VEM-reinforced epoxy, and (3) clay-loaded VEM reinforced epoxy", have been tested to check their Tg values by using DSC investigation, the result is presented in Table 2. These systems with adding amount of clay particles shows change in Tg values owing to the occurrence of clay nanoparticles, which declines the degradation percentage and affect the curing temperature. This could because the clay particles are made an interference with density of cross-link of epoxy chains [74,75].

Also, any raise in the addition of VEM material within system 1 leads to a decline in Tg values. This is attributed to the occurrence of stretchy groups, which leads to reduced cross-linking, interaction rate, and treating temperature. Hence generated an extra free volume of system 1 and shared to diminution the values of Tg temperature. The addition of clay particles into a composite of system 2 and production

nanocomposite (system 3) shared to reduce the values of Tg temperature, which attributed to the catalytic of the resin and plasticization of clay–loading resin matrices due to existing the "cetyltrimethylammonium ions" upper the surface of the clay material [76].

Table2 Thermal result of nanocompositesincluding (clay, VEM, and DGEBA) [76].

		TGA			
DGEBA/VE M/Clay composition	(O0) gT	Initial decompositio n (°C)	60% weight loss (°C)	Char yield (%) 800 °C	(%) IOT
100/00/00	160	352	417	12.6	22.5
100/05/00	177	340	403	7.8	20.6
100/10/00	171	354	413	16.5	24.1
100/15/00	168	363	426	23.7	26.9
100/00/01	150	348	433	24.3	27.2
100/00/03	156	356	438	26.1	27.9
100/00/05	161	363	445	31.5	30.1
100/10/01	162	360	449	21.7	26.2
100/10/03	159	368	451	25.2	27.6
100/10/05	152	371	464	29.8	29.5

Another matrix system [58] including (unmodified epoxy and a hybrid matrix of unsaturated polyester (UP) and epoxy) has been tested to investigate the (Tg) temperature, the result is represented in Table 3. The result showed a decrease in values of Tg temperature with expanding the addition of UP material. Also, this can be described due to the chain stretching and flexible property of UP resin. The addition of clay nanoparticles into the system of UP- epoxy matrix improved the Tg temperature values [77, 78] while the addition of clay nanoparticles into the epoxy matrix declined the values of Tg temperature. Again, the raise in the Tg temperature values can be distributed for the same reason to the ions of "cetyltrimethylammonium" in the gallery area of clay nanoparticles which declines the interaction rate and improved the curing temperature [79-81]. Hence, illustrates the good crosslink of clay nanoparticles with the matrix of UPepoxy of the nanocomposite system [58].

Table 3 Thermal result and water uptake of nanocomposites (hybrid UP–epoxy) [58].

Epoxy/UP/Cla y composition	Heat distortion temperature (°C)	Glass transition temperature (°C)	Water absorption (%)
100/00/00	155	166	0.1232
100/05/00	137	149	0.1197
100/10/00	131	142	0.1129
100/15/00	129	139	0.1068
100/00/01	141	153	0.1127
100/00/03	150	161	0.1021
100/00/05	154	165	0.0562
100/10/01	135	148	0.1103
100/10/03	146	157	0.1005
100/10/05	150	161	0.0539

Furthermore, the influence of clay type "Organo modified montmorillonite clay platelets" (OMMT) fillings on Tg temperature was studied [82]. The Tg temperature of the pure polymer was about 86 °C. But the manufacture of all composites leads to a decline in the Tg temperature, this decline was further considerable at minimal clay percentages.

Insignificant clay distribution occurred to decrease the interaction enthalpy of the polymer. Clay combination could work as a barrier through curing and barrier a more cross-linked arrangement, where minor d-spacing may prevent immigration of monomer units and oligomers into the occurred layers [82].

2.4 Flame Retardancy Property

Flame or fire is one of the environmental problems which can be barriers by using composite materials that have flameproof properties. This property has been studied in the unloaded Si-epoxy matrix and clay particles loaded in the Si-epoxy matrix, the flame retardancy property was estimated via the char yield from determining the values of their limiting oxygen index, LOI, (Table 3), through Krevelen's formula [83,84].

$$LOI=17.5+0.4s$$
 (3)

where s refers to the "polymer's char yield".

The result obtained from this equation gives the values of LOI, which agrees with developed flame retardance. For the system of Si-epoxy, the result

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showed that the value of the LOI was about 27.2. While the high value of the LOI was about in the range of 31.06 to 33.14 for the clay-loaded Si-epoxy system. A silane (SiH4) with a clay-loaded Si-epoxy system similarly presents greater values of LOI. Therefore, higher flame retardancy property is found in matrix systems with unloaded Si-epoxy matrix and (SiH4) with clay-loaded Si-epoxy matrix. The char protective influence of silicon presented the interactive influence on LOI improvement [84-85]. Other composite systems have been used to investigate flame retardancy, these composites including pure epoxy, "vinyl ester monomer (VEM)" loaded epoxy, and clay particles-loading VEMepoxy matrix, which is used to investigate the LOI property depending on the char yield [86, 87]. Flameretardant property, which is denoted as LOI, the value of this property is found to raise via the increase of the char yield. The result showed that the values of the system including clay-VEM-loading epoxy matrix had a higher value from other systems owing to the containing of an "inorganic nano-silica core group", which contributed to the stable thermal process [76].

2.5 Influence of liquids uptake and clay nanofiller on mechanical and thermal properties

The storage modulus has been studied by Berry et al. [88] for pure epoxy, they found that the value of the property declined with the time of exposure to water, this lessening was about 62percentage for 150 days. While the flexural strength and modulus have been studied by Alamri and Low [27] and they showed a decrease in these two properties after an exposure time of epoxy in water where the flexural strength was 12 per cent, and the modulus was 22 per cent. For polymer composite systems, reducing the amount of absorbed moisture can be useful for tools which have a direct connection with liquids such as water or humid environment places [88]. Some mechanical characterisations (tensile property as well as modulus of elasticity) of both unloaded epoxy and nanocomposite systems have been negatively influenced by the liquids uptake (water and oil) whereas another property such as the fracture strain has been a bit enhanced, this performance has relation to the quantity of liquid uptake [8]. The addition of clay nano loadings [28] to a polymeric matrix

produced from combined resources can affect some properties such as mechanical and thermal characteristics of clay-polymeric nanocomposite systems. As presented in Ref. [28], the Tg temperature of nanocomposite systems has been increased related to increased loading of clay particles percentage, this was estimated from measuring of dynamical mechanic investigations[89].

The influence of adding some types of clay nanoparticles on mechanical properties such as impact strength, elasticity, and fracture characteristics of nanocomposite system including а "ELO/ESO/epoxy" materials are investigated. Organo-clays of 5 wt% which own an exfoliated structure have led to improving some mechanical properties such as the storage modulus of about thirty per cent. While other properties such as the impact strength were reduced in the epoxy-nanocomposite system during the addition of organo-clays compare with the original system (epoxy) [90]. For another system, the flexural modulus nanocomposite increased by about thirty percentage due to its influence by adding 4 vol% from MMT clay nanoparticles, but without effecting other properties for example, Tg, stabile thermally, and flexural strength [91]. It is found that the elastic property, Tg temperature, and heat deformation degree similarly increased in the case of the additive clay nanoparticles about 5 wt% and linseed oil about 80 wt%. [92]. Additions of 2-3 wt% clay nanoparticles have led to making elastic properties, fracture strength, and stabile of heat temperature were improved [93].

Also, the tensile behaviour was expanded by about 100% due to the additive of clay nanoparticles amount of 2.5 wt%. A particular increase was noticeable in both elongation at fracture and force resistance under the effect of the existence of seed oil, this increase was owed to the assistance of seed oil to the increase the diffusing of the epoxy matrix within the interlayer spaces of the clay material [94, 95]. The addition of bentonite clay in a percentage of 4% influenced the tensile strength, of a system containing a nanocomposite, to be increased to 300 per cent [96, 97]. The toughness of the nanocomposite system was increased by about 75percentage during the addition of different clay percentages with epoxidized (10 wt%) in comparison with purely used polymer [98]. P-ISSN 1991-8941 E-ISSN 2706-6703 2023,(17), (1):112-128

Also, it is found that for nanocomposite systems, the storage modulus was increased by 400 per cent due to adding clay nanoparticles of about 2 wt%, this was influenced by some properties of nanocomposites such as the strength and stabile of thermal degree [99].

Conclusion

The environmental conditions have a scientific effect on the properties of nanocomposite materials during using them for the long term. The results of barrier properties as well as the mechanical and thermal characterisations of nanocomposites have been affected by surrounding conditions connected with adding clay nanoparticles and they showed different properties before exposing to environmental surrounding conditions. However, some conditions do not affect the result, for example, the environmental humidity has led to no significant variation in flexure modulus. Studying the effect of these conditions is important to achieve the requirement of the applications. Environmental problems can be barriers by using composite materials that have flameproof properties. Experience with polymer resins such as epoxy to UV energy has drawbacks to the creation of microcracks. The manufacture of all composites leads to a decline in the Tg temperature, this decline was further considerable at minimal clay percentages. These materials are showed their ability to barrier the environmental surrounding effects.

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تأثير الظروف البيئية وحبيبات الطين المضافة على خواص المتراكبات النانوية من الإيبوكسي – طين: مراجعة

قیس عبداللہ عباس

قسم الفيزياء، كلية العلوم، جامعة الانبار، الرمادي، الانبار، العراق.

الخلاصة:

في العقود القليلة الماضية ، أثبتت المركبات النانوية بما في ذلك أنظمة الجسيمات النانوية المصنوعة من الطين -ايبوكسي إمكانية تطوير خصائصها على مواد الاساس الأصلية. للظروف البيئية التي تحيط بأنظمة المركبات النانوية تأثير علمي على خصائصها أثناء استخدامها لفترة طويلة. لذلك ، فإن دراسة تأثير الظروف البيئية المرتبطة بإضافة حبيبات الطين النانوية على خصائص المركبات النانوية مهمة لتحديد متطلبات التطبيقات. تُستخدم المتراكبات النانوية في تطبيقات البنية التي نتعرض لأحمال ميكانيكية وتأثيرات حرارية أثناء تعرضها للظروف البيئية المحيطة والتي تشمل طاقة الأشعة فوق البنفسجية الكهرومغناطيسية والرطوبة وامتصاص الماء وبعض المحاليل القلوية. أظهرت هذه المواد قدرتها على منع التأثيرات البيئية المحيطة. انتشار السوائل في أنظمة المتراكبات النانوية من خلال تقريب (موديلات) مختلفة. ت على منع التأثيرات البيئية المحيطة. انتشار السوائل في أنظمة المتراكبات النانوية من خلال تقريب (موديلات) مختلفة. تضمن دراسة المراجعة هذه الجهد البحثي الذي تم إجراؤه على المتراكبات النانوية (حبيبات الطين النانوية من خلال تقريب وموديلات) مختلفة. تتضمن دراسة المراجبة أو خواص الجهد البحثي الذي تم إجراؤه على المتراكبات النانوية (حبيبات الطين النانوية من خلال تقريب وموديلات) مختلفة. تنضمن دراسة المراجبة أو خواص الماء وانتشارها في المتراكبات النانوية والتعرض لبيئات مختلفة: الإشعاع في نطاق الأشعة فوق البنفسجية ودرجة الرطوبة أو خواص مناقشة النطورات الحيلية.

الكلمات المفتاحية : بيئي ، طين إيبوكسي ، مركب نانوي ، امتصاص الماء ، خصائص حاجز